

CHARACTERIZING PEPTIDE ALPHA HELICES VIA COLD ION SPECTROSCOPY OF MODEL COMPOUNDS

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Tethered peptides are synthetic peptides in which a chemical linkage between two remote sites in the peptide sequence bind these sites together. The Fairlie group has devised a tether that locks the pentapeptide 'core' into a single turn of an alpha helix, robust to large swings in pH, temperature, and denaturant. By changing the chirality of the amino acids, left- (D) and right-handed (L) helices can be exclusively formed. Catenating these sub-units leads to α -helices of greater length. This talk describes the propensity of these tethered peptides to maintain their alpha helical nature upon the removal of solvent and transition into the gas phase as protonated ions. To this end we explore the structures of three tethered peptides linked together through the formation of a lactam between the lysine and aspartic acid residues, Y[KAAAD]-NH₂, F[KAAAD]-NH₂, and YR[KAAAD]-NH₂ (tether denoted by brackets). UV photofragment spectroscopy and IR-UV double resonance methods will be carried out on the cryocooled, protonated ions to probe the hydrogen bonding patterns of these molecules with the goal of elucidating the unique spectroscopic signatures of isolated single-turn alpha helices. The effect of the protonation site and handedness of the helix on the H-bonds in the single turn helices will also be described.